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A PRELIMINARY STUDY OF FACTORS AFFECTING THE CALIBRATION
STABILITY OF THE IRIIDIUM VERSUS IRIIDIUM-40 PERCENT
RHODIUM THERMOCOUPLE

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(NASA-TM-89086) A PRELIMINARY STUDY OF
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SUMMARY

A metallurgical study of iridium versus iridium-40 percent rhodium thermocouple was performed. The purpose of this study was to investigate the problems associated with the use of this thermocouple for high temperature applications (up to 2000°C).

The metallurgical studies included x-ray, macroscopic, resistance, and metallographic studies. The thermocouples in the as-received condition from the manufacturer revealed large amounts of internal stress caused by cold working during manufacturing. They also contained a large amount of inhomogeneities and segregations. No phase transformations were observed in the alloy up to 1100°C.

It was found that annealing the thermocouple at 1800°C for two hours, and then at 1400°C for 2 to 3 hours yielded a fine grain structure, relieving some of the strains, and making the wire more ductile. It was also found that the above annealing procedure stabilized the thermal emf behavior of the thermocouple for applications below 1800°C (an improvement from $\pm 1\%$ to $\pm 0.02\%$ within the range of test parameters used in this study).

INTRODUCTION

Measurement of settling chamber temperature and total temperatures in high temperature wind tunnel facilities, up to 1800°C, has been most commonly done with uncooled thermocouple probes. Platinum-rhodium alloy thermocouples have been used for measuring temperatures in the range 1300-1800°C. Measurement of temperature up to 2000°C in oxidizing atmospheres is possible with iridium-rhodium alloy thermocouples, although a number of problems affect their use. These problems include:

1. Lack of agreement with standard calibration tables.
2. Lack of agreement between thermocouples from the same lot of wire.
3. Change of calibration with time-in-service.
4. Susceptibility to breakage after high temperature exposure.

Change of calibration in service has been attributed to selective oxidation of iridium from the alloy (ref. 1). The iridium oxide then evaporates and leaves the wire, leaving a reduced iridium content. The selection of the 40 percent rhodium alloy for this investigation is based on the peak thermoelectric sensitivity of the iridium alloy occurring at 50 percent rhodium, so that the thermocouple will stay nearer its original calibration for a longer time. Also the melting point is higher for this alloy. The other factors are likely to result from manufacturing variables such as:

1. Addition of dopants to adjust the thermoelectric sensitivity of the thermocouple.

2. Addition of dopants to affect the crystal structure of the material so as to achieve better resistance to brittle fracture after high temperature exposure.
3. Variations in rhodium content in a given alloy melt.
4. Contaminants that occur during the melt phase and during the wire drawing phase.
5. Annealing of the wire, after fabrication.

Typical results at NASA Langley Research Center have shown a 10 percent lower thermoelectric sensitivity than the standard tables (ref. 2), and variations of up to 30 percent from these tables have been observed*. Since many of these problem areas associated with iridium versus iridium-rhodium alloy thermocouples have apparently not been studied, a study of the metallurgy of this thermocouple was undertaken.

BACKGROUND

When the junctions of two dissimilar metals forming a closed circuit are exposed to different temperatures, a net electromotive force is generated which induces a continuous electric current (Seebeck effect). The Seebeck voltage, E_s , refers to the net electromotive force set up in a thermocouple under zero-current conditions. This temperature difference between the junctions of the thermocouple always is accompanied by irreversible joule heating effects. The passage of the electric current always is accompanied by reversible heating or cooling effects at the junctions of the dissimilar metals (Peltier effect), while the combined temperature difference and passage of electric current always is accompanied by reversible heating or cooling effects along the conductors (Thomson effect).

The behavior of thermocouples is governed by three empirical laws. These laws are:

1. Law of homogeneous materials - no homogeneous conductor placed in a temperature gradient will generate a thermoelectric emf.
2. Law of intermediate materials - the algebraic sum of the thermoelectromotive forces in a circuit composed of any number of dissimilar materials is zero if all the circuit is at a uniform temperature.
3. Law of successive temperatures - if a thermocouple of homogeneous materials produces a thermal emf of E_1 , when the junctions are at temperatures T_1 and T_2 , and a thermal emf of E_2 , when the junctions are at temperatures T_2 and T_3 , the emf generated when the junctions are at T_1 and T_3 , will be $E_1 + E_2$.

"Homogeneous" means that the material composition is spatially uniform in all directions. Cold working, such as bending the conductors, or in fabricating the conductors, may be thought of changing the material density and varying the local homogeneity of a thermocouple conductor. Annealing the conductor is intended to relieve the stresses of fabrication and rehomogenize the conductors.

* Edwards, S. F., and Stewart, W. F.; Private Communications

METALLURGICAL STUDIES

The metallurgical studies were carried out on samples of iridium versus iridium-40 percent rhodium thermocouple in the as-received condition from the manufacturer. Unfortunately, no attempt was made in determining the purity of the samples. The metallurgical study consisted of four different phases:

1. X-Ray studies to identify the phases present.
2. Macroscopic studies to learn the macrostructure.
3. Resistance studies to investigate presence of phase transformations.
4. Metallographic studies to reveal the internal structure.

The as-received thermocouple samples were x-rayed in order to identify their phases, crystal structure, and lattice parameters. The x-ray diffraction analysis was conducted using a General Electric x-ray tube model XRD-IV operated using a copper target and a nickel filter. The analysis of the diffraction pattern of the as-received iridium-rhodium sample revealed it to be a single phase alloy of face-centered cubic crystal structure with a lattice parameter of 3.84 Å as indicated in table 1.

Macroscopic studies were carried out in order to study the macrostructure of the iridium-rhodium alloy. The as-received sample revealed a fiber texture indicative of directional flow of the grains along the longitudinal axis of the wire. It was found that a large amount of internal stresses caused by cold working during manufacturing were present in the alloy. The cold working was severe enough to have split the wire into several individual fibers as shown in figures 1 and 2. It is believed that these stresses would gradually anneal away upon exposure to high temperatures, resulting in a decrease in the thermal emf. An oxide film was observed on the surface of some fibers as shown in figure 3. The oxide film is believed to have resulted from either the material used in the processing, or the manufacturing process, or both.

The as-received sample was subjected to resistance studies in order to investigate possible phase transformations. The measurements were carried out only to 1100°C due to the experimental limitations. The results are shown in figure 4. There were some definite but small discontinuities at about 680, 835, and 1080°C. These discontinuities reflect the different stages of the annealing of residual strain. However, there were no indications of phase transformation within the temperature range studied.

Metallographic studies were carried out on polished and etched samples using a Leitz metallograph. The following elements were found suitable for the specific purposes indicated:

1. Electrolytic etchant - the electrolyte was dilute HCl (3-5 percent); etched at 0.06 to 0.1 Amp at 0.5 to 2 volts for 3 to 5 hours. It was used for revealing the general microstructure.
2. Fused-salt etchant - a mixture of 10 percent KNO_3 in KOH; etched by dipping for 5 to 10 minutes; was used for revealing the grain boundary structure.

3. Sodium chlorite solution - a saturated solution, etched by swabbing 2 to 3 minutes; was used for revealing the segregations and impurities. The as-received material was found to contain large amounts of segregations and inhomogeneities in some areas as shown in figure 5.

A black smoke emanated from the thermocouple wire when it was electrically heated. Some smoke, condensed on a cool glass slide, was analyzed by x-ray diffraction, and determined to be iridium oxide as indicated in table 2. Iridium oxide is highly volatile due to its vapor pressure, and escapes from the material upon heating. This effect results in a gradual loss of iridium from the alloy which alters its stoichiometric composition. The short lifespan of the thermocouple is mainly caused by the oxidation of iridium and volatilization of the iridium oxide. The pure iridium wire in the thermocouple oxidizes at a faster rate than the alloy, and is responsible for the catastrophic mechanical failure of the thermocouple.

The catalytic effect of iridium is expected to be present, particularly in an atmosphere of incomplete combustion. A considerable amount of information exists on the catalytic effect of noble metal thermocouples (refs. 3 and 4). However, no direct evaluation of the magnitude of the error in the resultant high reading of the thermocouple has been treated because of the multitude of the parameters involved in the analysis. Nevertheless, Olsen (ref. 5) has suggested that this error is a function of the type and amount of the combustible reactants, the homogeneity of the gas mixture, properties of the thermocouple, the condition of the wire, the contamination poisoning of the thermocouple wires, and lastly, the size of the wires.

ANNEALING STUDIES

The thermocouple samples were annealed so that the effect of heat treatment on their metallurgy could be studied. The samples were annealed in a high temperature furnace at the following temperatures and for the specified time intervals:

1. 1800°C for 1, 15, and 30 minutes.
2. 1900°C for 0.5, 1, 3, and 60 minutes.
3. 2000°C for 0.5, 1, 3, and 30 minutes.

Metallographic studies were performed on one of the thermocouples that had been annealed at 2000°C for 1 minute. The sample exhibited large recrystallized grains confined mostly to the surface as shown in figure 6. It is believed that this grain growth might be the cause of increased brittleness of the wires. The bright areas that appeared on some of the samples were believed to be zones of inhomogeneities and soluble impurities. These zones, which are believed to have lower melting points, migrate along the wire, and essentially disappear as the composition becomes uniform by the diffusional process of the atomic migration.

At all the annealing temperatures, there was nucleation of the recrystallized grains at different times, the time being shorter at higher temperatures. From a study of the percent recrystallized grains for the different cases, it was concluded that the incubation period of the recrystallization process is of the order of 30 minutes. This lower temperature was selected for the experimental advantage of controlling the heat treatment parameters with ease. To prevent possible excessive grain growth it was decided to heat treat the wires for two hours at 1400°C after

the initial annealing at 1800°C, and then cool the wires to room temperature in the furnace. The wire, annealed by this procedure was found to be ductile. The internal structure, shown in figure 7, consisted of fine grains with some black areas. These black areas were later identified by x-ray diffraction analysis to be iridium oxide. It was believed that some of the oxides were inherent in the alloy in its manufactured state, as was reported earlier, and that some oxides were formed during the annealing process. The oxide particles were distributed at random with a large percentage of them being located on the grain boundaries as shown in figure 8. X-ray studies and metallographic studies under polarized light revealed that most of the grains had random orientation. After separation of the iridium oxide lines, the alloy was determined, using x-ray techniques, to be a single phase, face-centered cubic crystal structure, as indicated in table 3, with a lattice parameter smaller than that found for the as-received sample. This difference is believed to be due to the release of the lattice strain in the annealed sample. Therefore, it was concluded that annealing the samples could cause pseudo-uniform internal structure, and randomize the grain structure.

EMF STUDIES

It was decided to investigate the effect of annealing on thermal emf stability. The studies were carried out on three samples of thermocouples annealed according to the following procedures:

1. Thermocouple #T1, annealed at 1800°C for two hours, then taken out of furnace and cooled in stagnant air to room temperature.
2. Thermocouple #T2, annealed at 1800°C for two hours, then step cooled in the furnace to 1400°C, then held at this temperature for three hours, and then taken out of the furnace and cooled in stagnant air to room temperature.
3. Thermocouple #T3, annealed at 1800°C for two hours, then step cooled in the furnace to 1400°C, then held at this temperature for three hours and then cooled in the furnace to room temperature.

The experimental arrangement included a Honeywell, strip chart recorder (Model Elektronik 194), a General Resistance voltage source (Model DAS-46A), a Keithley nanovoltmeter (Model 181), a Kay Instruments ice point reference standard, and a Consolidated Controls Corporation copper freezing point cell (Model FSP 505).

The experimental procedure included the annealing of the individual thermocouples in accordance with the specified heat treatments in a Thermogage paralytic graphite furnace which was controlled by an optical pyrometer. Then, each thermocouple was inserted in the well of the copper freezing point standard. After the copper was molten, it was allowed to freeze. A thermal analysis curve was recorded on the strip chart recorder, and simultaneous readings were taken at regular intervals with the nanovoltmeter. Thermocouple #T1 showed stability from run 6 to 11 (each run lasting for about 12 minutes) as shown in figure 9. Then, the thermocouple exhibited approximately a 1 percent decrease in emf from run 12 through run 14. Thermocouple #T2 exhibited a stable emf after 12 runs, the variation being less than 0.5 percent. A better result was demonstrated by thermocouple #T3 which exhibited a stable emf after 2 runs, the variation being 0.02 percent, as shown in figure 10. The difference between thermocouples #T2 and #T3 could be attributed to the difference in cooling methods used after their heat treatment. It is believed that thermal stresses were introduced in thermocouple #T2 by cooling it to room

temperature in stagnant air rather than in the furnace. The annealing and cooling method used for thermocouple #T3 not only generated pseudo-uniform internal structure with a randomized grain structure, but also managed to stabilize the thermal emf behavior of the thermocouple.

CONCLUSIONS

This study centered upon analyzing the metallurgy of iridium versus iridium-40 percent rhodium thermocouple wires. The as-received wires revealed a large amount of internal stress caused by cold working during manufacturing, and contained a large amount of segregations and inhomogeneities. No phase transformations in the alloy were observed up to 1100°C. The short lifespan of the thermocouple in high temperature applications was found to be mainly due to the oxidation of iridium, and the consequent volatilization of the iridium oxide. It was found then annealing the thermocouple at 1800°C for 2 hours, and then at 1400°C for 2 to 3 hours, would prevent excessive grain growth, thus yielding a fine grain structure; relieving some residual strains, and making the wire more ductile. It was found that this annealing procedure followed by cooling to room temperature in the furnace environment would stabilize to better than ± 0.02 percent the thermal emf of the thermocouple for applications below 1800°C.

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December 1986

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TABLE I.- X-RAY DIFFRACTION RESULTS OF THE AS-RECEIVED WIRE

Crystal Structure	face-centered cubic
Lattice Parameter	3.84 Å

Most intense line (i. e. $I/I = 100$ from (220) diffraction plane. The fiber axis is [220].

TABLE II.- X-RAY DIFFRACTION RESULTS OF THE "BLACK SMOKE"

Crystal Structure	tegragonal
Lattice Parameter	4.49 Å

Identified, by using Hanawalt's method and by consulting the International Powder Diffraction Index File, to be IrO_2 .

TABLE III.- X-RAY RESULTS OF THE ANNEALED WIRE*

Crystal Structure of the Alloy	face-centered cubic
Lattice Parameter	3.82 Å

Iridium dioxide diffraction lines were present. They were separated from other lines. The remaining lines were then indexed to give the results given above.

*At 1800°C for 2 hours and then 1400°C for 3 hours and furnace cooled.

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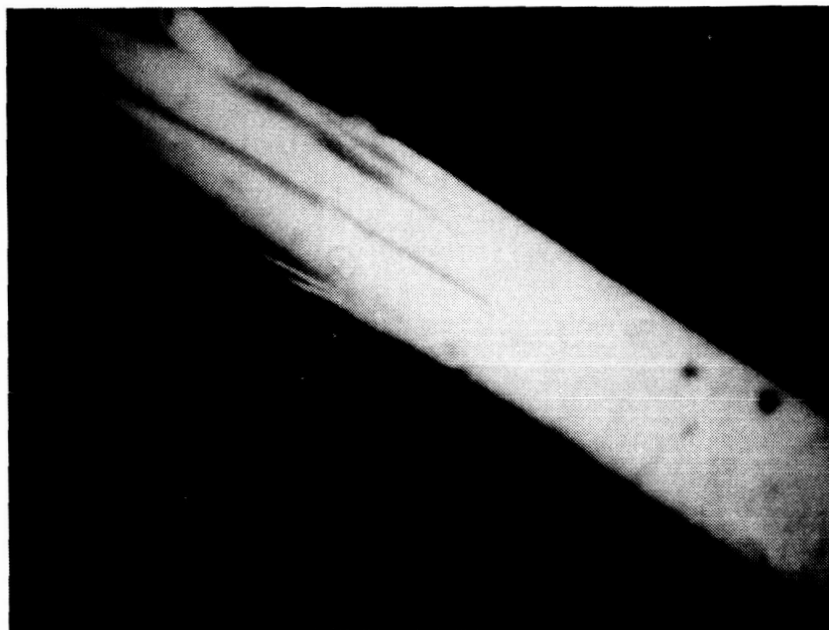


Figure 1.- Macrostructure of the as-received sample indicates work-hardening and directional flow. Note the separation of the grains due to work-hardening.

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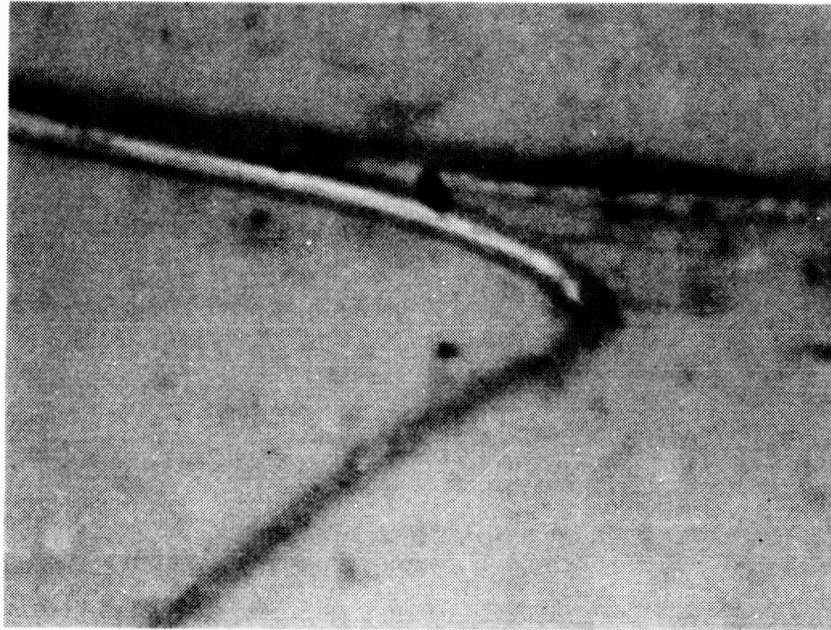


Figure 2.- Macrostructure of the as-received sample reveals 2 separated fibers.
Magnification: 100 x

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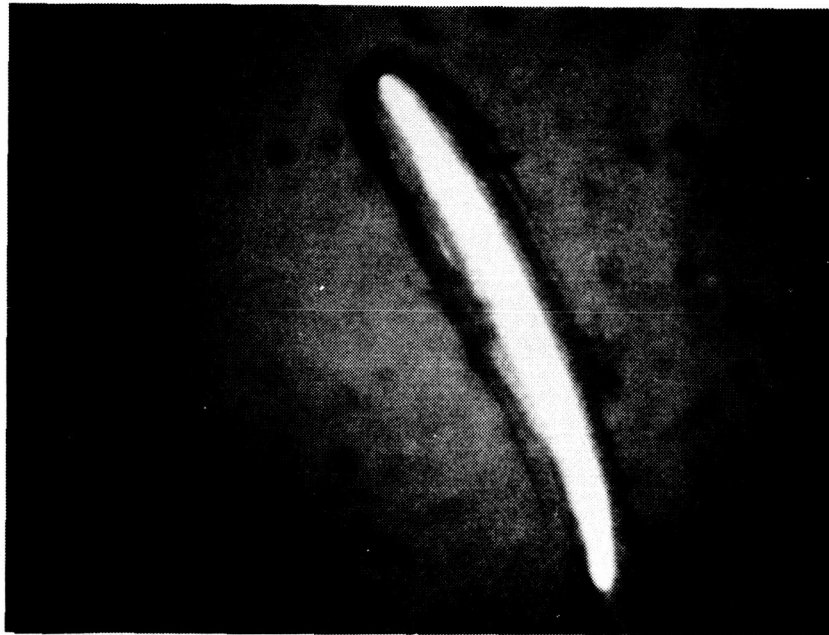
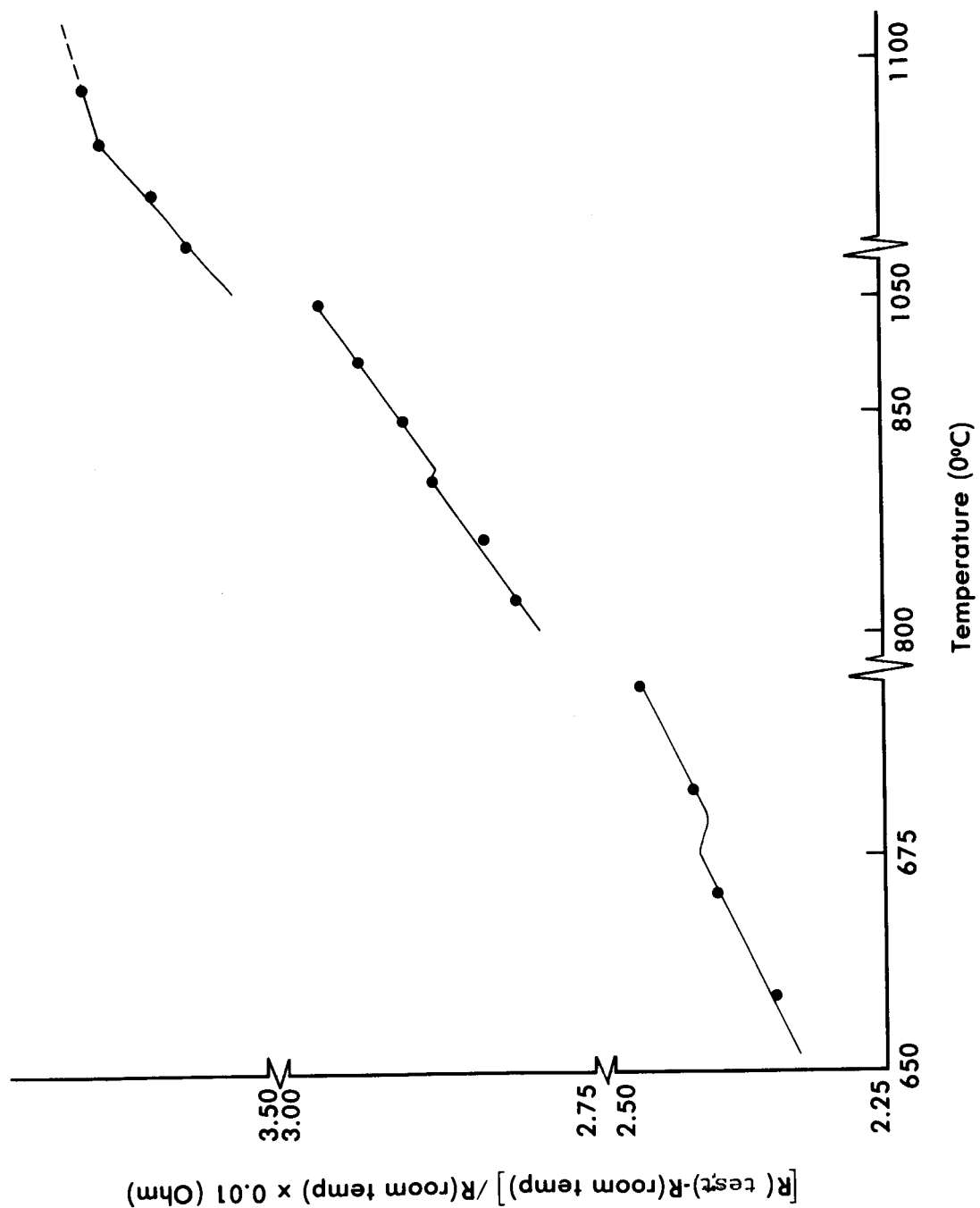


Figure 3.- Macrostructure of the as-received sample. Note the oxide layer around the fiber.
Magnification: 200 x



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Figure 5.- Microstructure of the as-received sample showing segregations and inhomogeneities. Etched surface.
Magnification: 200 x

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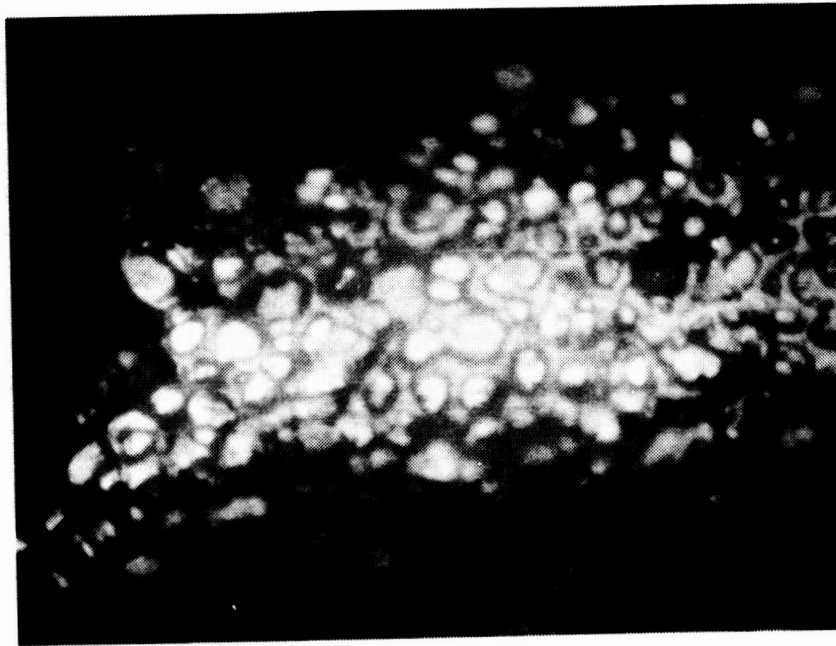


Figure 6.- Microstructure of a sample, heat-treated at 2000°C for 0.5 min.
Etched with special reagent to reveal recrystallized grains.
Magnification: 500 x

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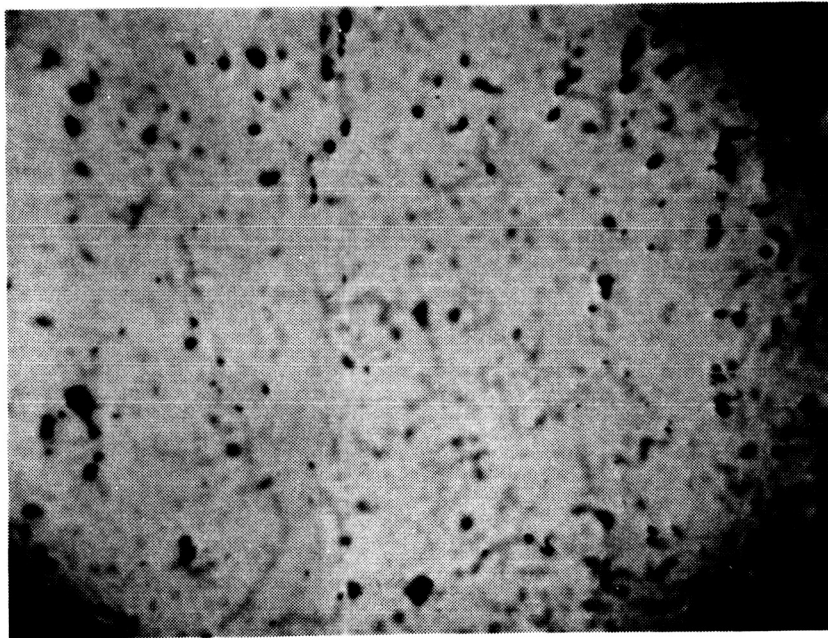


Figure 7.- The general microstructure of the annealed sample (see test), showing recrystallized grains, inhomogeneities and oxides.
Magnification: 500 x

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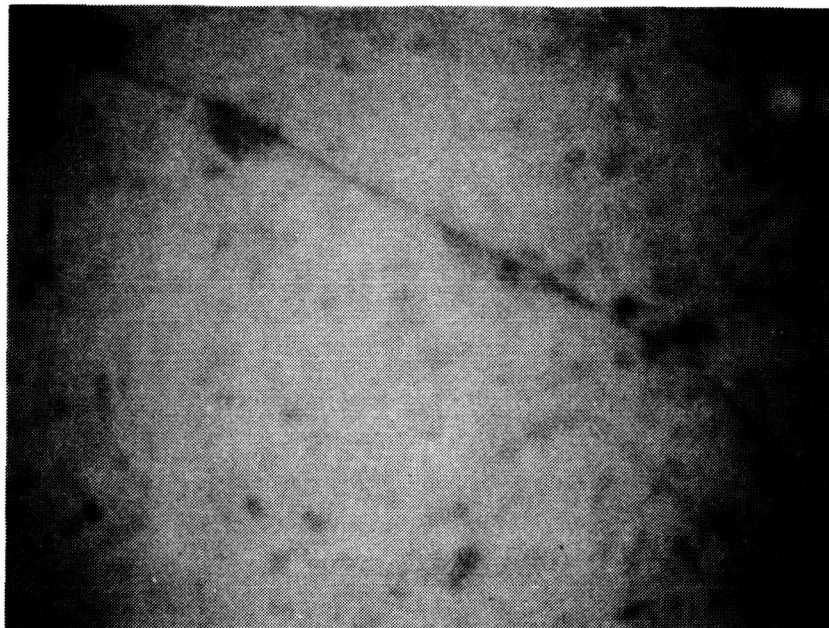


Figure 8.- Microstructure of an annealed sample showing 2 adjacent grains with the grain boundary where some oxide particles appear.
Magnification: 500 x

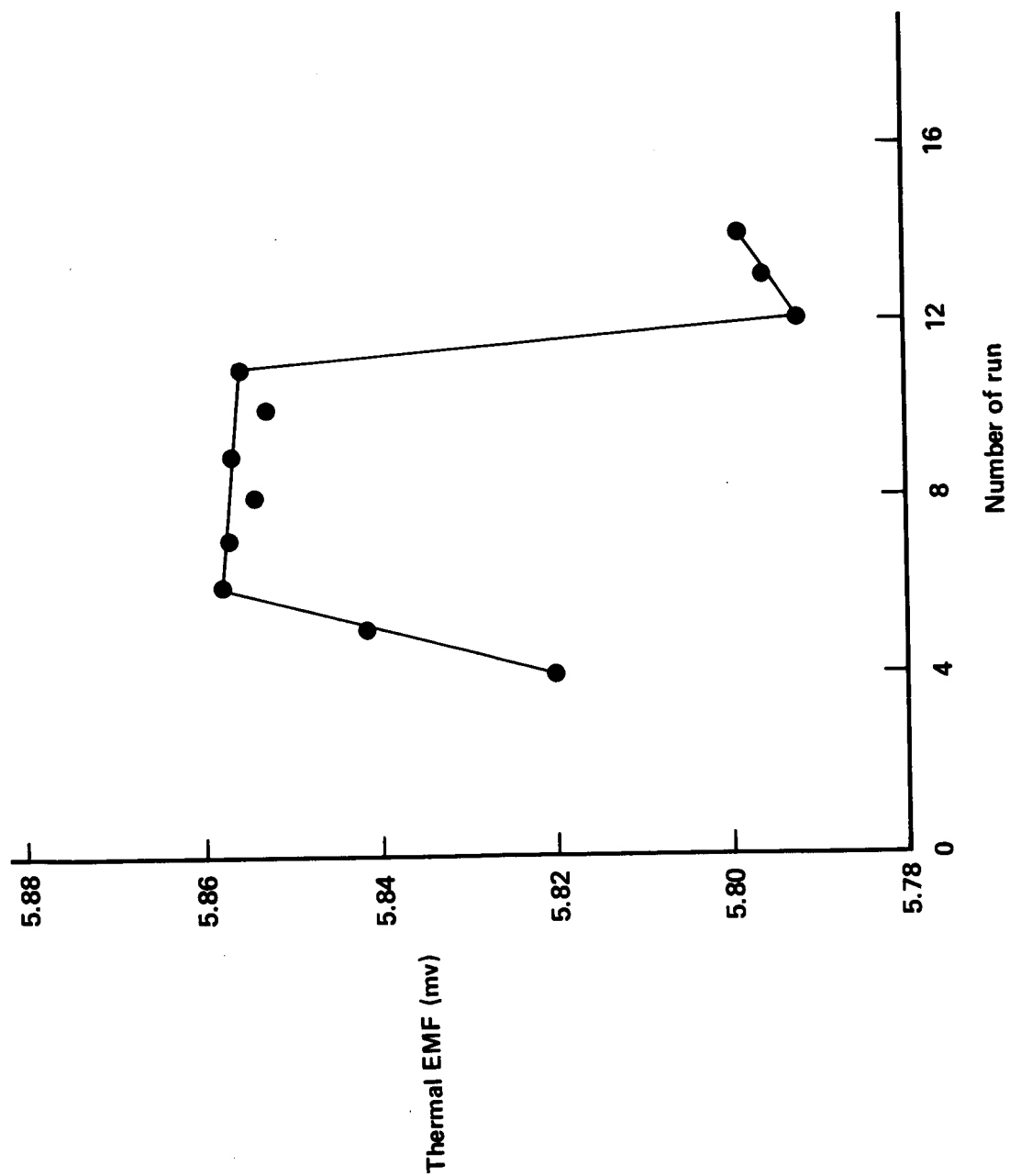


Figure 9.- EMF Stability of Thermocouple #T1 at 1083.3°C, each run lasting for 12 minutes.

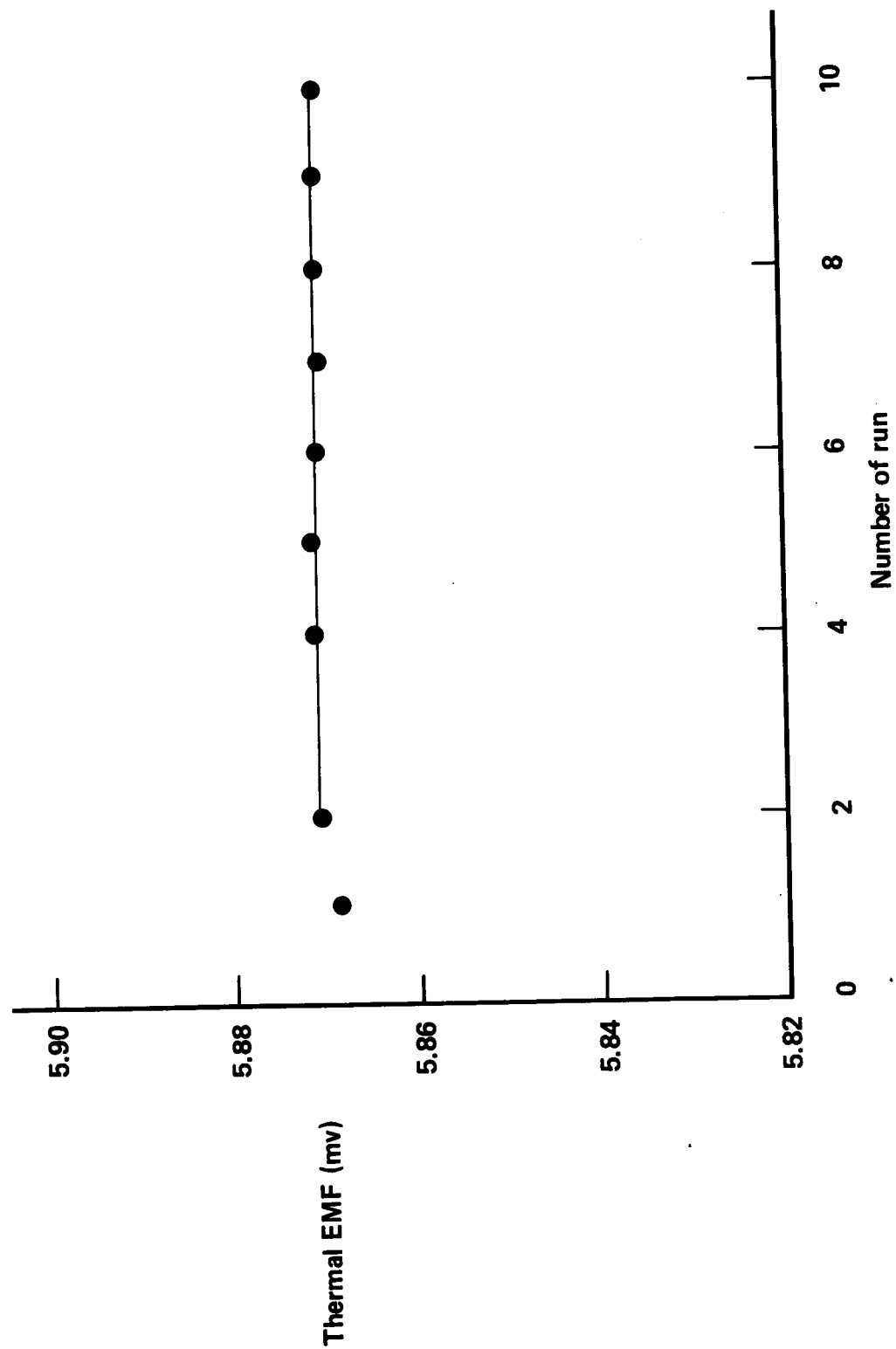


Figure 10.- EMF Stability of Thermocouple #T3 at 1083.3°C, each run lasting for 12 minutes.

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16. Abstract A metallurgical study of iridium versus iridium-40 percent rhodium thermocouple wires was performed. The thermocouple in the as-received condition from the manufacturer was found to have large amounts of internal stress, segregation and inhomogeneity. It was found that specific annealing procedures could relieve some of the internal strains. This procedure also improved the stability from ± 1 percent to ± 0.002 percent over the temperature range tested.					
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